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## ***In situ* mass spectrometry and ion chemistry in the stratosphere and troposphere**

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### **I. INTRODUCTION**

Ions are generated in the atmosphere by a variety of ionization processes. These include photoionization, collisions with energetic particles and cosmic rays, and at ground level ionization from energetic particles released from radioactive decay of radon and other gases (1-10). Although the ionization process varies, the primary ions are usually similar. The primary ions result from ionization of the abundant neutrals  $N_2$  and  $O_2$  producing  $N_2^+$ ,  $N^+$ ,  $O_2^+$ , and  $O^+$ . A notable exception is the ionization of NO by Lyman  $\alpha$  near the mesopause. The subsequent chemistry is then controlled by less abundant neutrals. As will be shown later, neutrals in the part-per-quadrillion range can affect the ion composition. Ions are lost by recombination with electrons or ions, and in the lower atmosphere loss to surfaces such as aerosols and the ground becomes important.

The ion density varies between about  $10^3$  and  $10^6$  ions  $m^{-3}$ . At altitudes below 100 km, the ionization density is relatively constant (3). The ion density varies by less than a factor of 10 from  $10^3$  ions  $cm^{-3}$ , even though the neutral density changes by a factor of approximately  $4 \times 10^6$ . Therefore the mixing ratio of ions to neutrals decreases substantially from high altitude to low altitude. At the ground level there is only 1 ion (or less when large concentrations of aerosols are present) for approximately every  $10^{16}$  neutral molecules. Because of the large decrease in the mixing ratio of ions, mass spectrometric measurements of the ion composition are more difficult at lower altitudes. This difficulty outweighs the opposing difficulty in using the various *in situ* measuring platforms. In order of increasing altitude, the measuring platforms are trailer, aircraft, balloon, sounding rocket, and satellite. As a result, the ion composition of the upper atmosphere has been measured before that of the lower atmosphere, and in fact the last portion of the atmosphere where *in situ* measurements have been made is the troposphere.

In discussing the ion composition of the atmosphere it is useful to discuss a high-pressure region below 100 km and a low-pressure region above 100 km, in part due to the presence of three-body processes becoming important at high

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pressure and therefore lower altitudes. The main features of the chemistry of the low-pressure region have been known for many years and are the subject of numerous reviews and will not be discussed here (1-10). In contrast, the *in situ* ion composition measurements of the stratosphere and especially the troposphere have come about relatively recently, and progress is continually being made. The recent progress is due to a variety of reasons. Once instrumentation was developed to make these measurements, the platforms, such as trailers, aircraft, and balloons, were stable and allowed long-duration measurements. Another very important reason is that ion composition measurements of the stratosphere, troposphere, and other parts of the atmosphere have proven in recent years to be valuable in determining the neutral composition of the atmosphere.

This review will concentrate on the ion chemistry of the stratosphere and troposphere since it is in this region that most progress has been made in the past decade. This is especially true in the instrumentation used for the measurements, and a discussion of the instrumentation will start the review, with emphasis given to the evolution of the measuring techniques. This will be followed by a discussion of the ion chemistry of the stratosphere and troposphere. Finally, the use of ion composition measurements to derive trace neutral concentrations will be discussed. The emphasis of this section will be to relate advances in the instrumentation to new capabilities.

## II. INSTRUMENTATION

Most of the mass spectrometric measurements of the ion composition of the atmosphere (excluding space experiments) have been made with quadrupole mass spectrometers. The exception is the magnetic instrument developed by Kopp at the University of Bern (11-14). The instrumentation used in rocket-borne mass spectrometry has been discussed in detail by Arnold and Viggiano (1), and the present review will emphasize lower-altitude measurements and new details for the rocket instrumentation.

In the stratosphere and troposphere only quadrupole-based systems have been used. These systems vary in detail and have undergone a large increase in complexity in recent years. The basic system, as in any mass spectrometer, consists of the quadrupole(s), a pumping system, a detection system, associated electronics, and the sampling system. The detection systems for all instruments have been electron multipliers of standard design and will not be further discussed. The remainder of this instrumentation discussion will be divided into two sections: the flight-based systems of the Max-Planck-Institut für Kernphysik group in Heidelberg (MPI-K) and the trailer-based systems of the Georgia Institute of Technology (GIT) group. These are the two groups currently making measurements in the lower atmosphere.

Besides the above two groups, there have been other active researchers in *in situ* mass spectrometry, especially in the upper atmosphere. The first measurements in the atmosphere on a rocket were by Narcisi and co-workers (15-19) at the Air Force Cambridge Research Laboratory (20). This work continues on sounding rockets, with particular emphasis on measurements during chemical

releases (21, 22). Other rocket measurements were made by Kopp and co-workers at the University of Bern (11-14), Goldberg and co-workers at NASA Goddard (23-25), and Arnold and Krankowsky at the MPI-K (26-28). Previously, measurements in the stratosphere on balloon platforms were made by the group of Arijs and co-workers at the Belgium Institute of Space Technology (29-38). Experiments on satellites are beyond the scope of this review.

### A. Flight Instruments

The main reason quadrupole mass spectrometers designed to be flown on aircraft, balloons, and rockets differ from laboratory instruments is the weight and power requirements associated with the various flight instruments. This is most true for rocket-based instruments and least true for aircraft instruments.

A critical part of the weight restriction is the pumping system. The subject of flight pumps has been reviewed in detail previously (1), and only a brief summary is given here. The lightest efficient pumps are cryopumps, and these are now used for all instruments, although a titanium sublimation pump has been used in the past (39). The first flight instrument used a liquid-nitrogen-cooled zeolite pump (40). It suffered from a relatively low pumping speed, especially after an extended-length flight.

Liquid-helium-based pumps replaced the nitrogen-based system and offered excellent pumping speed (1, 26). The main drawback of the helium-cooled systems is that liquid helium has a low heat capacity. Therefore the pump either needs to be large or the flight time needs to be short. Short flight times sufficed for rocket instruments but had the disadvantage that the instrument needed to be filled just before launch, limiting the time response to short-lived phenomena.

In order to overcome the difficulties related to helium-cooled cryopumps, the MPI-K group started using a liquid-neon-cooled pump (41, 42). Liquid neon has the advantage of a heat capacity per unit volume of approximately 40 times that of liquid helium. Even though liquid neon is much more expensive on a per volume basis than liquid helium, the costs per unit heat capacity are similar. The only drawback of liquid-neon-based systems is that they do not pump neon (20 ppm) and helium (5 ppm) very well. These gases are found in only small abundances in the atmosphere and therefore the neon-based pumps are an ideal solution for the short flights of rocket instruments. For the longer flights possible on balloons and airplanes, liquid-neon-based pumps degrade due to a buildup of neon and helium.

Two "tricks" have been used in order to improve the pumping of these trace gases. The first is the use of charcoal sorbent located in a chamber of the pump connected to the main chamber only by a small channel (43). The idea is that the main gases in the atmosphere are pumped in the main chamber, while the secondary chamber with the charcoal sorbent then pumps the neon and helium without pumping a lot of nitrogen and oxygen. This delays saturating the sorbent. The pumping speed is on the order of  $3000 \text{ l s}^{-1}$  (43). In practice, this works rather well for several hours, but after that time the secondary chamber's efficiency deteriorates and the pressure in the instrument increases. The MPI-K

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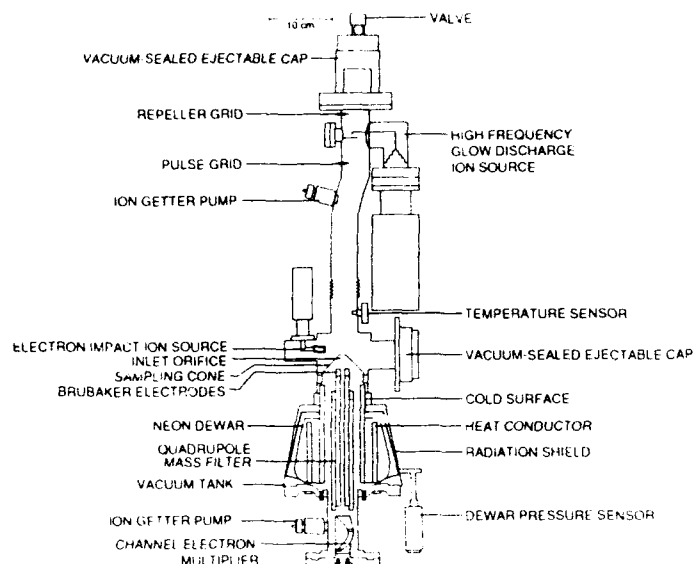
group has solved this problem in a very simple manner (44, 45). They attach to the main instrument an empty volume ( $400\,000\text{ cm}^3$ ) many times larger than the mass spectrometer chamber. Since the flux of neon and helium is fixed by the sampling orifice, the total flux of the light gases is the same but spread over a larger volume, thereby reducing the pressure. This simple solution now allows for long flights without any significant degradation of performance due to poor pumping. An additional benefit is that the increased volume allows a larger volume of gas to be "pumped." This allows a larger inlet orifice and greater ion flux. Kreiger and Arnold (44) estimate as much as a 25-fold increase in the sensitivity due to the added volume.

The first quadrupoles for flight instruments were small in size in order to decrease the weight and power requirements. The small quadrupoles associated with these instruments meant decreased resolution and to some extent sensitivity. The first stratospheric data had very broad peaks (43, 46, 47). Newer instruments use larger rods similar to those found in laboratory instruments. Typically, the rods in the new instruments are 1.6 cm in diameter and 20-30-cm long (44, 48). This new generation of instrument has a mass range up to 100 amu and is capable of unit mass resolution up to this value.

Most of the Heidelberg data were taken with quadrupoles with open front ends and no lens between the sampling orifice and quadrupole. Ions were drawn in only by the field axis potential of the quadrupole. This resulted in some collisional dissociation of weakly bonded cluster ions (49). More recently, a Brubaker lens has been added to the front of the quadrupole, and sensitivity has increased (50). They have also developed a triple quadrupole system but have not as yet published any data taken with that instrument (51).

For aircraft and balloon measurements, sampling of ions occurs simply through a small hole in the front blunt plate of the mass spectrometer housing. The hole size is adjusted for maximum sensitivity, which depends on altitude and pumping speed of the cryopump. On faster-moving platforms such as rockets and parachutes, the front plate needs to be replaced by a cone in order to assure good flow dynamics around the sampling region (41-43, 46, 47). A flow tube was added to the sampling system for the airplane measurements in order to take outside air into the region of the mass spectrometer (52). Only the airplane's velocity is used to flow the atmospheric gas. For recent balloon measurements incorporating a flow tube, a small turbine pump has been added (45, 53). The sampling port of the mass spectrometer is positioned perpendicular to the gas flow. A rocket instrument has also recently had a flow tube added and a schematic of this instrument is shown in Fig. 1 (54). In this case, the flow is directed at the nose cone of the rocket mass spectrometer. The airplane instrument is quite similar except that the flow direction is perpendicular to the sampling orifice, and the balloon instrument has the turbine pump added to aid the gas flow in the tube.

A major advance in recent years has been the development of active ionization sources. In this technique ions are created external to the mass spectrometer by any of a number of methods. The first attempts involved the placement of filaments in front of the stratospheric balloon instruments. The use of a flow tube on the airplane instruments allowed for a more controlled situation. Ions



**Figure 1.** Rocket-borne mass spectrometer flown by the group of Frank Arnold at the Max-Planck-Institut für Kernphysik.

were created at the beginning of the flow tube and allowed to react for a time determined by the flow velocity in the tube. The typical reaction length is approximately 70 cm, and the residence time has varied from 17 to 140 ms. These times are measured in flight by pulsing a grid and looking at the change in the ion current at the sampling plate. This technology has not been used extensively on other platforms such as balloons (45,53) and rocket-borne parachute (54) instruments. The ion source can vary but is typically a high-frequency glow discharge such as shown in Fig. 1

Each of the platforms mentioned throughout this section covers only certain sections of the atmosphere. Airplane measurements can be made from ground level to about 10–15 km. Special research aircraft such as the ER-2 are capable of reaching 20 km but are expensive to fly and flight time is limited. Balloon measurements cover the range from 15 to 45 km. The lower limit is set so that the balloons do not interfere with airplane traffic. Only very large and expensive balloons of approximately  $1 \times 10^6 \text{ m}^3$  reach altitudes of 40–45 km. Sounding rockets have been used for measurements above 60 km. Below 60 km the atmospheric pressure is too high for good sensitivity measurements at a sounding rocket's velocity. For a time the region between the upper balloon altitudes and lower sounding rocket altitudes was essentially inaccessible. This altitude is now covered by sounding rockets attached to parachutes (rocket-borne drop sonde) (55). In this technique, a low apogee of 60–70 km is set for the sounding rocket. Just before apogee a parachute is opened. This has several advantages over conventional rockets. Lowering the speed allows for longer measurement times. The parachute orients the rocket and therefore the mass spectrometer in the direction of the flow, which is critical for good sampling of

various instruments are housed in trailers, although an instrument capable of airplane measurements is under development. The present generation of instruments has been greatly improved since the first measurements were made in the early 1980s (58, 59). The mass spectrometer part of the instrument is relatively standard. Both single and triple quadrupoles are used, with a triple quadrupole shown in the drawing. The triple quadrupole is used for collision-induced dissociation studies for species identification. The detector is a standard channel electron multiplier. Since size, weight, and power requirements are relaxed when making ground-based measurements, the pumps are normal diffusion pumps. Other parts of the instrumentation are also of more conventional design due to the absence of flight-based restrictions.

The ion sampling is anything but standard and has some very clever and unique features. Ions enter a large sampling scoop designed to reduce turbulence (59). The scoop is connected to a sampling tube. An ion source is located at the entrance to the sampling tube. Tesla coils, x rays, and discharge ion sources have been used. This allows for sampling of recently ionized species as well as ambient ions and allows the evolution of the ion composition to be studied.

The sampling tube is a flow opposed drift tube, the first of the unique features related to the ion mobility heritage. The air is pulled through the drift tube by a blower. The drift tube is composed of a series of concentric metal rings, isolated from each other and connected by a series of resistors. This produces a uniform electric field. The field is used to slow down the ions, which has the effect of increasing the concentration of ions. The field is weak enough in this region so that the ions remain thermal. In experiments where ions are created by the ion source, the field can be varied to control the residence time, adding to the versatility of the instrument. The varied residence time allows for study of the ion evolution and helps identify important reactions. Perhaps more importantly, it allows for good control of conditions when trace gas concentrations are to be derived from the ion composition measurements, as described in the next section.

At the end of the drift tube, the ions are extracted from the main air flow by a weak transverse electric field and enter another high-pressure ion optics region. At the upstream end of this region a dry nitrogen or argon buffer is added. The ions flow against the buffer and are focused into the vacuum entrance aperture by a series of focusing rings. By the time the ions enter the first vacuum chamber, four different types of high-pressure ion optics have been used: the drift tube, deflection rings, extracting rings, and focusing rings. The use of such a variety of high-pressure ion optics is a result of the ion mobility background.

Essentially all ions in the troposphere are cluster ions of some type, i.e., composed of a core ion with any number of ligands. In the lower atmosphere, the high pressure and large concentration of water vapor leads to a situation where the number of water ligands can be large. The usual case is that the identity of the core ion is much more interesting and relevant than the exact ligand distribution. The presence of ligands makes core identification difficult by spreading the charge over a large number of masses. Even if it were desired, measuring the distribution of the weakly bonded ligands is very difficult. In

sampling from a high-pressure gas it is easy to dissociate weakly bonded species in the fields of the mass spectrometer or to promote clustering in the free jet expansion. For all these reasons, the GIT group has concentrated on identifying core ions. Several techniques are used to desolvate the atmospheric ions. The first part of the desolvation procedure is the use of the dry buffer gas referred to previously. This has the effect of dehydrating ions since water is the main ligand at ground level due to the high concentration of water vapor. It also prevents the rapid hydration of ions which would otherwise form in the vacuum entrance aperture. Other ligands may also be lost to varying extent.

Immediately following the vacuum entrance aperture is the collisional dissociation chamber. This part of the apparatus is optional and best described in a 1986 paper (60). The collision dissociation chamber is in essence another drift tube; this one operates at pressures on the order of 0.1–1 Torr. The lower pressure in this drift tube allows for much higher energy collisions than are possible in the sampling drift tube. In this region, the ions undergo between 10 and 100 collisions at an applied  $E/N$  of 0–800 Td (1 Td =  $10^{-15}$  V cm<sup>2</sup>). For studying clusters and cluster growth 0–100 Td is used. These conditions are sufficient to remove most if not all of the ligands when desired. Core ions were found to dissociate only at the highest fields (>700 Td), and a value of 250 Td is the nominal value used to remove water ligands. The earlier work did some crude core identification by dissociating ions in this region (60). Subsequent work has relied on the triple quadrupole for the core identification studies (61–63).

Upon leaving the low pressure drift tube the ions enter a vacuum optics chamber run at approximately  $10^{-3}$  Torr. The vacuum optics are of standard design. Finally, the ions enter the triple quadrupole region. The mass spectrometry and detection techniques are standard and will not be further discussed.

The above describes only the basic instrument. Newer models have been designed to make measurements of specific neutral trace gases with ultrahigh sensitivity. These include atmospheric-pressure-selected ion chemical ionization mass spectrometry. This new technique makes use of a multistage ionization technique which completely isolates the sampled air from the ionization region. A specific ion species is created and injected into the sampled air and allowed to react for a specific time. This prevents metastable and radical species formed in the ionization region from entering into the neutral-detection chemistry. Neutrals that have been detected by this technique include sulfuric acid, methanesulfonic acid, dimethylsulfoxide, and sulfur dioxide (64, 65). An extension of this technique allows the sampled gas to pass through a gas chromatograph and thereby monitors the reaction of a single ion species with a single gas (65). This powerful technique will undoubtedly yield many interesting and important results.

The most impressive achievement to date is the detection of the very important OH radical. A 5-min integration time results in a sensitivity of  $7 \times 10^4$  molecule cm<sup>-3</sup> (66, 67). For nighttime measurements a longer integration time of 60 min is typical and the sensitivity is  $2 \times 10^4$  molecule cm<sup>-3</sup>. This technique involves titration followed by atmospheric-pressure-selected ion

chemical ionization mass spectrometry. Discussion of this technique will be delayed until the results section since it requires a better knowledge of the ion chemistry of the lower atmosphere than has been given so far.

### C. Laboratory Measurements

A detailed knowledge of the processes involved in the ion chemistry of the atmosphere requires not only *in situ* measurements but also laboratory studies of the kinetics and chemistry. In fact, it is the interplay between the laboratory work and *in situ* measurements that allows sensitive detection of the neutrals involved in the ion chemistry. This interplay will be shown in the results section. The laboratory measurements have almost exclusively been made in flowing afterglows and selected ion flow (drift) tubes. These experimental techniques have been the subject of numerous reviews and the interested reader is referred to them (68, 69).

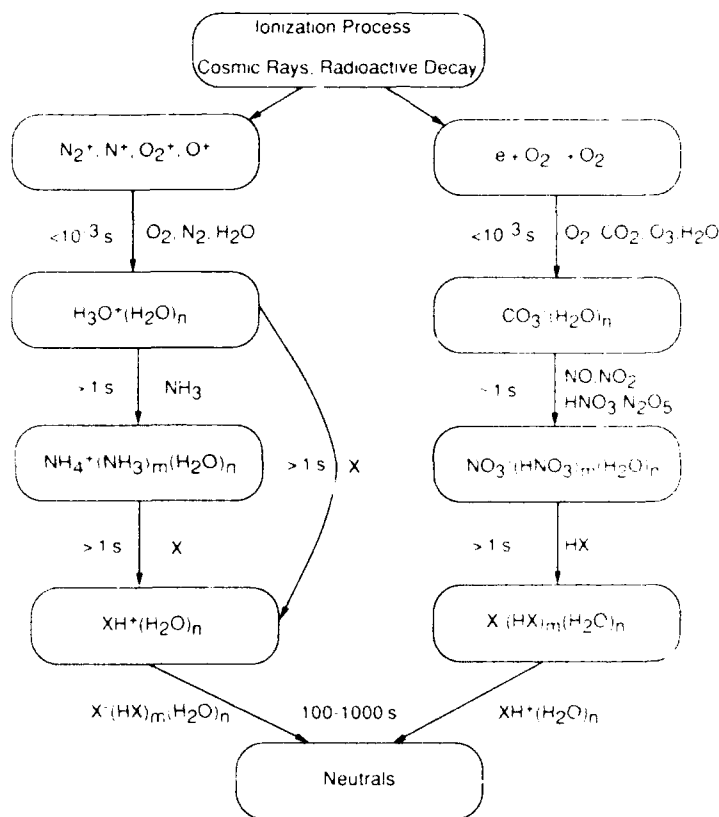
## III. ION CHEMISTRY OF THE LOWER ATMOSPHERE

The ion chemistry of the lower atmosphere can be divided into a number of stages. The initial ion chemistry is similar to that found in the upper atmosphere but occurs much faster. The upper atmospheric ion chemistry has been known for a long time (1-10) and will only be discussed in passing here. As stated in the Introduction, the primary charged particles formed in the lower atmosphere are  $N_2^+$ ,  $O_2^+$ ,  $N^+$ ,  $O^+$ , and free electrons (2). The free electrons are converted rapidly to negative ions mainly by three-body attachment to  $O_2$  to form  $O_2^-$ . A very schematic representation of the ion chemistry of the lower atmosphere is given in Fig. 3. Only the most important processes are given, and rough estimates of the time scales involved are given as well. More detailed descriptions are given in the reviews referred to above.

For positive ions, a series of well understood reactions involving  $O_2$ ,  $N_2$ , and  $H_2O$  lead to the relatively stable series of ions  $H_3O^+(H_2O)_n$ , where  $n$  peaks around 3-5. The time scale for this conversion varies with altitude, but in the stratosphere and troposphere the conversion can be considered complete in about  $10^{-3}$  s. This is much shorter than the ion-ion recombination lifetime (which normally controls the ion residence time) of approximately 100-1000 s. For all practical purposes, the series of ions  $H_3O^+(H_2O)_n$  can be considered as primary ions in the positive-ion chemistry since the chemistry leading to this series is so rapid.

For negative ions, the primary ions are quickly converted into  $CO_3^-(H_2O)_n$  ions by a series of reactions with  $O_2$ ,  $CO_2$ ,  $O_3$ , and  $H_2O$ . The time scale for this conversion is again on the order of  $10^{-3}$  s. In the undisturbed atmosphere, the  $CO_3^-(H_2O)_n$  ions are converted relatively slowly into the more stable ions  $NO_3^-(HNO_3)_n$  by reaction with the trace gases NO,  $NO_2$ ,  $HNO_3$ , and  $N_2O_5$ . The time scale for this conversion is on the order of 1 s in the stratosphere and considerably faster in the troposphere.

Once the ions  $NO_3^-(HNO_3)_n$  and  $H_3O^+(H_2O)_n$  are formed, the chemistry becomes that of Brønsted acids and bases, i.e., all subsequent reactions involve



**Figure 3.** A schematic representation of the ion chemistry of the stratosphere and troposphere. Time scales shown are very approximate and are used only as a guide.

proton transfer except for ligand switching and association reactions. The latter reactions leave the core ion unchanged.  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  will therefore react only with trace compounds that have a proton affinity greater than that of  $\text{H}_2\text{O}$ . Reaction will produce species of the form  $\text{HX}^+(\text{H}_2\text{O})_m$ . The number of ligands transferred will depend on the proton-affinity difference. However, the distribution of  $\text{H}_2\text{O}$  ligands quickly reaches an equilibrium concentration due to the relatively high water concentrations found in the lower atmosphere. For compounds that have a proton affinity only slightly larger than that of  $\text{H}_2\text{O}$ , essentially all the ligands must be transferred to keep the reactions exothermic. In fact, when the proton-affinity difference is small, the different bond strengths of the ligands to the core ions can change the direction of the exothermicity. If the concentration of  $\text{X}$  is large, species such as  $\text{H}^+(\text{X})_n(\text{H}_2\text{O})_m$  may be formed by ligand exchange of  $\text{X}$  for  $\text{H}_2\text{O}$ . These ions can then react further with species of even higher proton affinity. A good example is at ground level, where  $\text{NH}_4^+$  ions are formed in high abundance and subsequently react with other amines, such as pyridine and picoline, among others

(57, 59, 60, 62). This is shown in Fig. 3 as the only branch from the main sequences.

Similarly for negative ions it is the proton-affinity difference or more commonly the gas-phase acidity difference that drives the chemistry after  $\text{NO}_3$  cores are formed. Only Brønsted acids that are more acidic than  $\text{HNO}_3$  will react with  $\text{NO}_3$  ( $\text{HNO}_3$ )<sub>n</sub>. Examples are  $\text{H}_2\text{SO}_4$  (43, 47) and  $\text{CH}_3\text{SO}_3\text{H}$  (61, 63).

The compounds that react with the stable ions  $\text{NO}_3$  ( $\text{HNO}_3$ )<sub>n</sub> and  $\text{H}_2\text{O}$  ( $\text{H}_2\text{O}$ )<sub>n</sub> are usually found only in very small abundances. Many of the chemicals that do react with the ions were not predicted to exist in the atmosphere, and ion composition measurements were the first to show their existence there. One of the first examples is  $\text{CH}_3\text{CN}$  (acetonitrile), which has been found to play an important role in the ion chemistry of the stratosphere, though found in only minute quantities (34, 46, 70).

In summary, after only a small fraction ( $\sim 0.1\%$ ) of the lifetime of an ion, the ion chemistry becomes rather simple. The only processes that occur are proton transfer, ligand switching, and association. Despite this simplicity, a variety of neutrals play a role in the chemistry. Only two main series of negative ions are found in the stratosphere,  $\text{NO}_3$  ( $\text{HNO}_3$ )<sub>n</sub> and  $\text{HSO}_4$  ( $\text{H}_2\text{SO}_4$ )<sub>n</sub> ( $\text{HNO}_3$ )<sub>n</sub>. The former series represents the dominant ions throughout much of the stratosphere and troposphere. The latter series is dominant in the region between 30–50 km (29, 33, 35, 37, 43, 47, 55, 71–76). While these two series comprise the vast majority of negative ions in the stratosphere, additional ligands such as  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{HNO}_2$ , and  $\text{HOCl}$  are also found. At altitudes near ground level, additional series of ions are also found. The core ions for these series are  $\text{CH}_3\text{SO}_3$  and  $\text{C}_3\text{H}_3\text{O}_4$ , resulting from deprotonation of methanesulfonic acid and malonic acid, respectively (57, 59–63).

In the stratosphere, the main series of positive ions are  $\text{H}_3\text{O}^+$  ( $\text{H}_2\text{O}$ )<sub>n</sub> and  $\text{H}^+$  ( $\text{CH}_3\text{CN}$ )<sub>n</sub> ( $\text{H}_2\text{O}$ )<sub>n</sub> (30, 32, 33, 36, 46, 52, 77–82). Particularly stable is the ion  $\text{H}^+$  ( $\text{CH}_3\text{CN}$ )<sub>n</sub> ( $\text{H}_2\text{O}$ ). It is only in the lower stratosphere and troposphere that other bases play a major role in the stratospheric positive-ion chemistry. Near the tropopause protonated acetone and methanol enter into the chemistry (36, 79).

Near ground level, the starting series of positive ions is  $\text{NH}_4^+$  ( $\text{H}_2\text{O}$ )<sub>n</sub> rather than  $\text{H}_3\text{O}^+$  ( $\text{H}_2\text{O}$ )<sub>n</sub>. Therefore only species that have a proton affinity larger than that of  $\text{NH}_4^+$  (204 kcal mole<sup>-1</sup>) enter into the ion chemistry. Even with this restriction, a larger number of species play a role in the positive-ion chemistry in the troposphere, particularly at ground level. It is mostly amines and related compounds (57, 59, 60, 62, 63) that are involved since these are the compounds that have higher proton affinities than that of  $\text{NH}_4^+$  (83). Frequently, whole series of compounds are involved. One of the main series includes pyridine and the methyl- and ethyl-substituted pyridines, such as picoline. Another series is that starting with ammonia and continuing to trimethylamine. More exotic species such as quinolone and caprolactam as well as a series that appears to be methyl-substituted glucoses with one amine group also occur at ground level. The species have been identified by tandem mass spectrometer experiments (57, 59, 60, 62, 63). At higher altitudes in the troposphere protonated ammonia and pyridine still play a role but decrease in importance at higher altitudes.

This is because the abundance of the precursor gases decreases due to incorporation into droplets followed by rainout.

The fact that both the positive- and negative-ion chemistry of the atmosphere proceeds in very discrete steps with time scales separated by orders of magnitude allows for very sensitive detection of the trace neutrals involved in the chemistry. In the next section, examples of neutral detection by ion composition measurements will be given. Particular attention will be paid to the interplay between laboratory measurements of the kinetics involved and the *in situ* ion composition measurements. It is the goal of trace neutral detection that has driven some of the most important advances in *in situ* ion composition measurements.

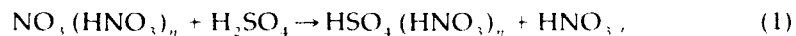
#### IV. TRACE NEUTRAL DETECTION BY ION COMPOSITION MEASUREMENTS

The list of trace neutral concentrations derived from ion composition measurements is now relatively long. In this section, several of the techniques used for deriving the trace neutral concentrations will be given. Emphasis will be placed on the more important neutral species as well as technique development, which is now very sophisticated. Finally, at the end a quick summary of the other species and the techniques used to derive them will be given.

The first compound to be discussed is  $\text{H}_2\text{SO}_4$ . This is a good starting point since  $\text{H}_2\text{SO}_4$  was one of the first chemicals to be extensively studied in the stratosphere by ion composition measurements. The same chemistry involved in  $\text{H}_2\text{SO}_4$  detection is also used for OH measurements at the ground level.

The first measurements of the stratospheric negative-ion composition showed two main series of negative ions,  $\text{NO}_3(\text{HNO}_3)_n$  and one identified at the time as  $\text{R}(\text{HR})_n(\text{HNO}_3)_n$ , where HR was at the time an unidentified acid of mass  $98 \pm 2$  amu (47). Arnold and Henschen speculated that HR was sulfuric acid ( $\text{H}_2\text{SO}_4$ ). There were two prerequisites to confirm this identification. The atmospheric mass spectra had to be improved to allow for unambiguous mass identification, and laboratory measurements of the relevant chemistry had to be made.

Two main questions were posed for the laboratory work: (a) Does  $\text{H}_2\text{SO}_4$  react with  $\text{NO}_3(\text{HNO}_3)_n$ ,  $n = 0-2$ ,

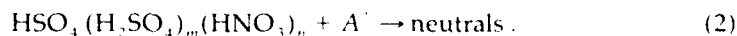


and (b) What is the rate constant for reaction (1)? Studies of the chemistry of  $\text{H}_2\text{SO}_4$  are difficult because  $\text{H}_2\text{SO}_4$  has a very low vapor pressure and is very corrosive. The group at the NOAA Aeronomy Laboratory made a study of these reactions in a flowing afterglow (84, 85). The  $\text{NO}_3(\text{HNO}_3)_n$  ions were generated from  $\text{HNO}_3$ . For this study, one of the normal flowing afterglow inlets was replaced with a furnace containing a small amount of  $\text{H}_2\text{SO}_4$  on some glass wool. Dry  $\text{N}_2$  was passed through the furnace, saturating the gas with  $\text{H}_2\text{SO}_4$ . In a setup like this the flow rate of  $\text{H}_2\text{SO}_4$  was proportional to the square root of the nitrogen flow. While absolute rate constants could not be measured since the vapor pressure of  $\text{H}_2\text{SO}_4$  was not known accurately, relative rate constants

for a number of ions were determined. However, the rate constants were put on an absolute basis by realizing that the rate constants for many of the reactions were collisional. The rate constant for the fastest reaction was then set equal to the collision rate. The study showed that reaction (1) proceeded rapidly for  $n = 0-2$ . The rate constants for  $n = 0$  and 1 were collisional and that for  $n = 2$  slightly less. Therefore  $\text{H}_2\text{SO}_4$  was likely to be the HR proposed by Arnold and Henschen (47).

In subsequent flights, Arnold (72, 86) and Arijs (35, 37) and their co-workers pinpointed the mass of HR as 98 amu. Therefore the assignment was correct.

The rather simple chemistry involving  $\text{H}_2\text{SO}_4$  in the stratosphere provided a convenient means not only for detecting the presence of  $\text{H}_2\text{SO}_4$  but also for deriving its concentration. Reaction (1) is the only reaction in the atmosphere that produces  $\text{HSO}_4$  core ions. There is no other atmospheric acid that is stronger than  $\text{H}_2\text{SO}_4$ , and therefore there is no chemistry that changes the  $\text{HSO}_4$  core. Association and ligand switching reactions do occur leaving the terminal ions as  $\text{HSO}_4(\text{H}_2\text{SO}_4)_n(\text{HNO}_3)_m$ . Consequently, in the absence of surfaces where condensation can occur, the only loss process for ions with  $\text{HSO}_4$  cores is ion-ion recombination,



Since there is only one production and one loss process for  $\text{HSO}_4$  core ions, a simple steady state on reactions (1) and (2) yields the concentration of  $\text{H}_2\text{SO}_4$  as

$$[\text{H}_2\text{SO}_4] = \frac{[\text{HSO}_4]\alpha\text{A}^+}{[\text{NO}_3]k} \quad (3)$$

where  $[\text{HSO}_4]$  and  $[\text{NO}_3]$  are the number densities of all ions with  $\text{HSO}_4$  and  $\text{NO}_3$  cores, respectively,  $\alpha$  is the ion-ion recombination rate constant,  $\text{A}^+$  is the total positive-ion density, and  $k$  is the rate constant for conversion of  $\text{NO}_3$  cores to  $\text{HSO}_4$  cores [reaction (1)]. For the purpose at hand, it is assumed that all ions with  $\text{NO}_3$  cores convert into  $\text{HSO}_4$  cores with the same rate. The laboratory measurements show that this is approximately true. More accurate measurements can be obtained by multiplying specific rate constants by specific concentrations. The ratio of ions with  $\text{HSO}_4$  cores to those with  $\text{NO}_3$  cores is measured *in situ* by mass spectrometers. Notice that only relative concentrations need to be measured.

Laboratory measurements are needed for  $\alpha$  and  $k$ . As explained previously, the rate constant for reaction (1) has been measured. Rate constants for numerous ion-ion recombination reactions have been studied in the laboratory. Most of the relevant data have been taken by the flowing afterglow Langmuir probe technique developed at the University of Birmingham by Smi. and Adams (87-89). Fortunately, it has been shown that complex ions, such as those found in the atmosphere, all recombine with approximately the same rate constant of  $(5-8) \times 10^{-8}$  molecule  $\text{cm}^3 \text{s}^{-1}$ . Thus an average value can be used for  $\alpha$ .

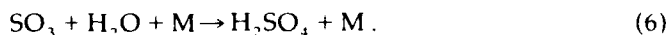
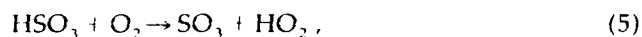
The total positive-ion density can be measured *in situ* by various techniques,

or previous values can be used since the density does not vary much over time because the cosmic-ray ionization process is relatively stable. There is a solar cycle variation, but this can be accounted for.

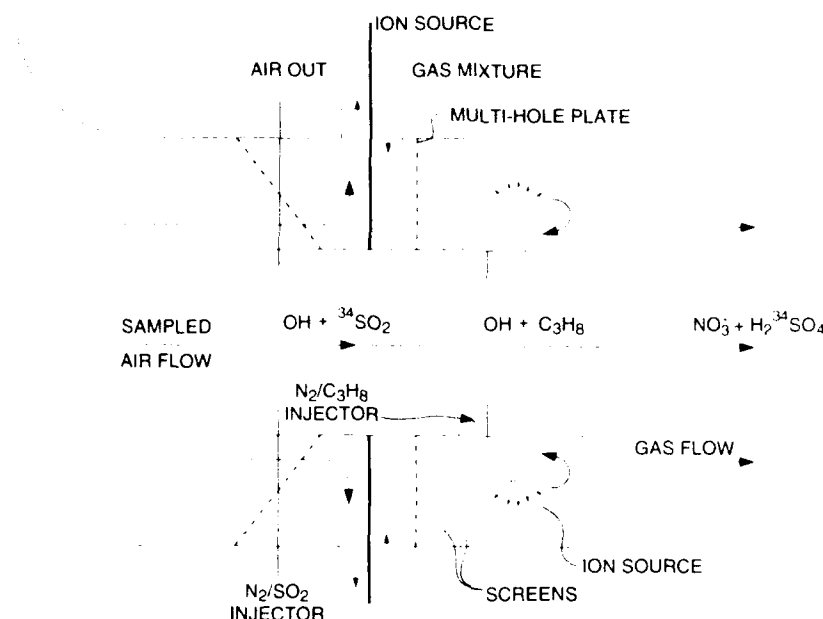
Therefore all the information needed to derive the atmospheric gas-phase  $\text{H}_2\text{SO}_4$  concentration is at hand when *in situ* ion composition measurements are made. The accuracy of the derivations is about a factor of 2–3 while the precision is much better, on the order of tens of percent. Employing this technique,  $\text{H}_2\text{SO}_4$  concentrations have been measured as a function of altitude over most of the lower atmosphere (29, 31, 50, 64, 76, 90–94). Concentrations as low as  $10^4 \text{ cm}^{-3}$  have been found, and the sensitivity would allow concentrations considerably smaller than this to be derived. The extreme sensitivity stems from the fact that the ion-ion recombination lifetime is on the order of 100–1000 s, thereby allowing reaction (1) a long time to occur. In the troposphere where  $\text{SO}_2$  and other sulfur gas concentrations are locally elevated, species other than  $\text{H}_2\text{SO}_4$  appear to lead to  $\text{HSO}_4^-$ . For this situation  $\text{H}_2\text{SO}_4$  is allowed to react exclusively with  $\text{NO}_3$ ,  $(\text{HNO}_3)(\text{H}_2\text{O})_n$  on a 0.1–0.2-s time scale and  $[\text{H}_2\text{SO}_4]$  is calculated from the  $\text{HSO}_4^-/\text{NO}_3$  ratio and the product of  $kt$ . At present this is the only way to measure gas-phase  $\text{H}_2\text{SO}_4$  concentrations even though  $\text{H}_2\text{SO}_4$  is quite important in controlling the stratospheric aerosol layer and acid rain.

A very important extension of this technique has recently been introduced by the GIT group in order to measure OH concentrations (64, 66, 67). This is one of the most important trace neutral species in the atmosphere and very difficult to measure, although much effort has gone into its measurement through optical means. The ion-assisted measurements have required significant enhancements to the basic measurement system described above.

A schematic of the inlet system for these measurements is shown in Fig. 4. Air is sampled through a turbulence-reducing scoop into a tube approximately 20-cm long and 10 cm in diameter. The flow velocity is about  $70 \text{ cm s}^{-1}$ . Shortly after entering the flow tube, the center of the air flow is made turbulent through introduction of  $\text{N}_2$  through two opposed injectors. The amount of  $\text{N}_2$  added is about 0.5% of the total gas. About 0.01% of isotopically labeled  $^{34}\text{SO}_2$  is added with the nitrogen. The  $^{34}\text{SO}_2$  converts OH into  $\text{H}_2^{34}\text{SO}_4$  by the following series of reactions:



Conversion takes place in a time on the order of 0.02 s. The rate-determining step is reaction (4). After conversion of >95% of the OH into  $\text{H}_2^{34}\text{SO}_4$ , the reaction is stopped by addition of  $\text{N}_2/\text{C}_3\text{H}_8$  into the flow tube. The  $\text{N}_2$  again is added as a turbulence producing gas and  $\text{C}_3\text{H}_8$  is added because it reacts with OH.  $\text{C}_3\text{H}_8$  is added in sufficient quantity so as to quench reaction (4) before entering into the ion-reaction region, but otherwise unaffected the chemistry.



**Figure 4.** Schematic representation of the inlet system used in OH measurements of Fred Eisele's group at the Georgia Institute of Technology.

In order to check the background,  $C_3H_8$  is added in place of the  $SO_2$ . The above chemistry effectively converts OH into  $H_2^{34}SO_4$  on a nearly one-to-one basis. A correction can be made for unconverted OH.

After the neutral chemistry is complete, the flow is allowed to become laminar and the  $H_2^{34}SO_4$  is detected by reaction (1). The ion source used in the initial experiments ionized air by a  $\beta$  source in the gas stream. The normal atmospheric ion chemistry converted the ions into  $NO_3$ . This source had several problems that are eliminated by the present design. These include OH production in the source, slow production of  $NO_3$  in very clean air (low concentration of  $NO_3$ -containing species) and contamination by other ions besides  $NO_3$ .

Presently, the ions are made externally to the main flow of gas in an outer coaxial layer of sheath air. Ions are produced by a 5-MeV  $\alpha$  source. The  $\alpha$  source has the advantage of being short range and keeps the ion production local. The sheath gas is comprised of filtered air with a small amount of  $HNO_3$ . The  $HNO_3$  reacts with all ions produced from air except  $HSO_4^-$ ,  $CH_3SO_3^-$ , and  $C_3H_3O_4^-$  (malonate) to produce  $NO_3$ -containing ions, predominantly  $NO_3^-$  ( $HNO_3$ ). The non- $NO_3$  ions are produced only slowly from their corresponding protonated trace neutral and are not a problem except that the small amount of  $H^{34}SO_4$  produced from ambient  $H_2SO_4$  results in a small background since  $H^{34}SO_4$  is the ion used for OH detection. The  $H^{34}SO_4$  background is determined by adding  $C_3H_8$  in place of the  $SO_2$ . Once formed the  $NO_3$  ( $HNO_3$ ) ions are forced

into the central gas flow by electric fields and allowed to react with the  $\text{H}_2^{34}\text{SO}_4$  for about 0.1–1 s. The use of an external ion source allows for very controlled chemistry and keeps any OH production by the ion source isolated from the reaction region. Ions are sampled by a mass spectrometer similar to that described for the ambient ion composition measurements.

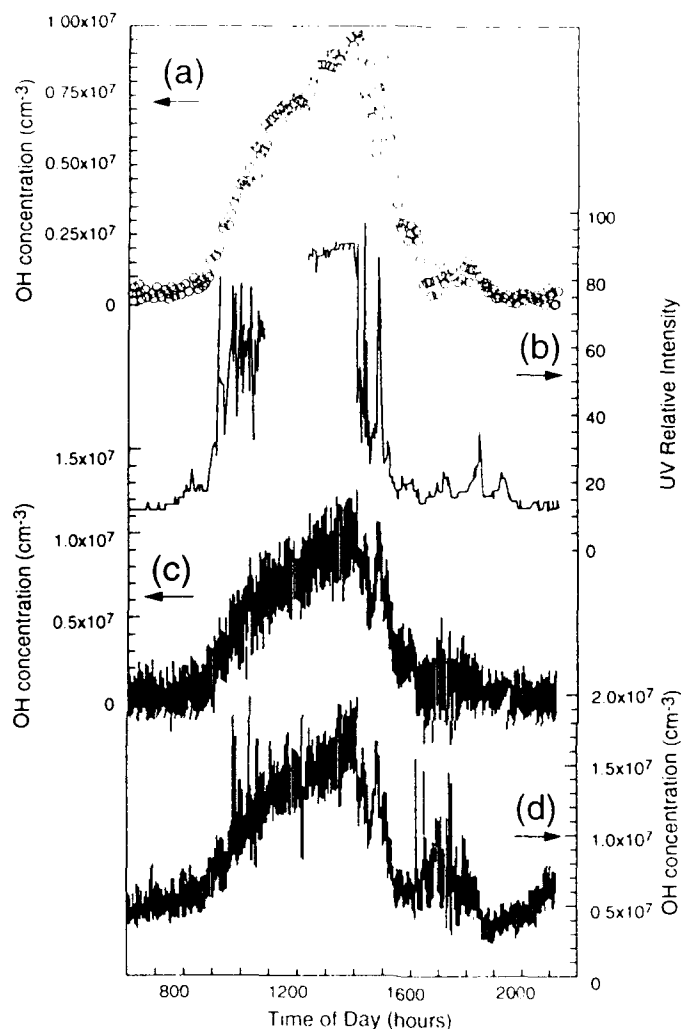
The  $\text{H}_2^{34}\text{SO}_4$  concentration and therefore the OH concentration are given as

$$[\text{OH}] = [\text{H}_2^{34}\text{SO}_4] = \frac{[\text{H}^{34}\text{SO}_4]}{[\text{NO}_3]kt}, \quad (7)$$

where  $t$  is the reaction time between  $\text{NO}_3$  and  $\text{H}_2^{34}\text{SO}_4$  and  $k$  is the rate constant for reaction (1) with  $n = 1$ . Alternatively, the CIT group has calibrated the instrument by detecting OH spectroscopically. The results agree with the above technique within experimental error. The present sensitivity is in the low to mid  $10^4$  molecule  $\text{cm}^{-3}$  range, and measurements can be made in tens of seconds. An example of the data obtained in this manner is given in Fig. 5 along with the solar UV flux which produces OH. Note the quick response of the data to the solar UV changes.

The elaborate injection system can be easily modified to allow detection of other trace neutrals. Allowing the  $\text{NO}_3$  ( $\text{HNO}_3$ ) ions to react with ambient air rather than chemically treated air allows detection of  $\text{H}_2\text{SO}_4$ ,  $\text{C}_3\text{H}_4\text{O}_4$  (malonic acid), and  $\text{CH}_3\text{SO}_3\text{H}$  (methanesulfonic acid) (64).  $\text{NO}_3$  ( $\text{HNO}_3$ ) reacts with all three neutrals by proton transfer with or without ligand transfer. These are the only three ambient gases that react with  $\text{NO}_3$  ( $\text{HNO}_3$ ). The concentration of these gases is determined by equations similar to Eq. (7). Reaction time is kept short so that only about 1% of the  $\text{NO}_3$  ( $\text{HNO}_3$ ) ions are converted to the product ions  $\text{HSO}_4$ ,  $\text{C}_3\text{H}_4\text{O}_4$ , and  $\text{CH}_3\text{SO}_3$ . The small amount of conversion ensures that no subsequent chemistry of the product ions occurs, e.g., reaction of  $\text{C}_3\text{H}_4\text{O}_4$  with  $\text{H}_2\text{SO}_4$  among other possibilities. This technique has been employed in conjunction with the OH measurements and separate  $\text{SO}_2$  measurements to track the sulfur chemistry at ground level (64). The sensitivity limit is in the parts per quadrillion range.

A little thought yields many other possibilities for measuring a variety of trace neutrals. Substitution of  $\text{NO}_3$  ( $\text{HNO}_3$ ) ions by  $\text{NH}_4^+$  ions yields concentrations of strong bases such as DMSO (dimethyl sulfoxide) (95). A potentially very powerful addition is a gas chromatograph to the air inlet system. The pre-separation removes compounds that may mask the chemistry of the species of interest. This technique has been used successfully for  $\text{CH}_3\text{SCH}_3$ ,  $\text{SO}_2$ , and  $\text{C}_{15}\text{H}_{24}$  ( $\beta$ -caryophyllene) (65). The ions used for detection of these neutrals are  $\text{H}^+$  ( $\text{H}_2\text{O}$ ) $_n$ ,  $\text{O}_3^+$  ( $\text{H}_2\text{O}$ ) $_n$  and  $\text{CO}_3^+$  ( $\text{H}_2\text{O}$ ) $_n$ . In general,  $\text{H}^+$  ( $\text{H}_2\text{O}$ ) $_n$  ions can be used to detect any compound with a proton affinity higher than about 170 kcal mol $^{-1}$  and  $\text{O}_3^+$  ( $\text{H}_2\text{O}$ ) $_n$  ions can be used for species with electron affinities higher than about 44 kcal mol $^{-1}$ . Either laboratory measurements of the relevant chemistry or an instrument calibration is needed to quantify the results accurately. It is easy to see that many such possibilities should exist and that the potential of this technique is just beginning to be exploited. The present development of an airborne system will also enhance the capabilities immensely.

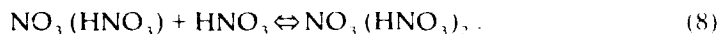


**Figure 5.** An example of data showing OH concentrations derived from ion mass spectrometry. Measurement of (a) OH concentration (300 s integration time), (b) UV solar flux (which produces OH), (c) OH concentration (10 s integration time), and (d) raw OH concentration (5 s integration time and no background subtraction). Reprinted with permission from F.L. Eisele and D.J. Tanner *J. Geophys. Res.*, **1991**, 96, 9295, copyright by the American Geophysical Union.

Although it is possible to give numerous additional examples of trace gas detection, only one more will be discussed in detail, namely, that of nitric acid. This gas is chosen for two reasons. First, the technique for measuring its concentration has evolved. Also, it is a very important species in polar ozone chemistry.

The first determination of the concentration of  $\text{HNO}_3$  from ion composition

measurements was published in 1980 (96). Rather than relying on steady state between ion production and loss as for  $\text{H}_2\text{SO}_4$ , this determination of the concentration of  $\text{HNO}_3$  relied on the following equilibrium:



The concentration of  $\text{HNO}_3$  is given simply as

$$[\text{HNO}_3] = \frac{[\text{NO}_3(\text{HNO}_3)_2]}{[\text{NO}_3(\text{HNO}_3)]K} \quad (9)$$

where  $K$  is the equilibrium constant for reaction (8). The ion ratio is easy to determine from the ion composition measurements, and the equilibrium constant had been measured in a flowing afterglow system at NOAA (97). The interplay between laboratory measurements and *in situ* measurements is again easily apparent. While this technique yielded  $\text{HNO}_3$  concentrations, it suffered from several problems. Equilibrium had to be established, which means that the  $\text{HNO}_3$  concentration had to be large enough for equilibrium to occur. No fragmentation of the weakly bonded ion clusters could be tolerated. The temperature must be known accurately since a 4° error in temperature results in a factor of 2 error in the  $\text{HNO}_3$  concentration derived. These conditions are assured to be met only over a narrow altitude range above 35 km.

A second attempt at deriving nitric acid concentrations was made by Viggiano and Arnold in 1981 (43). This method was based on a steady state for the production and loss of  $\text{NO}_3(\text{HNO}_3)$ . The production processes are



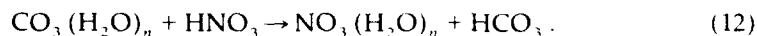
and



Essentially all other atmospheric negative ions come from  $\text{NO}_3(\text{HNO}_3)$ . The loss processes are ion-ion recombination and reaction with  $\text{H}_2\text{SO}_4$ . A little thought shows that the loss rate can be equated to the ion-ion recombination rate of  $\text{NO}_3(\text{HNO}_3)$  and all ions that are formed from it. Values of the rate constants for reactions (10) and (11) were estimated to be about the same as those used for the first measurements involving this technique (43). The rate constant for reaction (11) has since been measured (98, 99). The  $\text{HNO}_3$  concentration derived from this method was in approximate agreement (factor of 2) with the equilibrium method discussed above. Heitmann and Arnold later used this method in the upper troposphere (73). This method also had shortcomings. Possibly the most important was that the precursor ions  $\text{NO}_3$  and  $\text{NO}_3(\text{H}_2\text{O})$  are only found in small abundance at most altitudes, and therefore measurements were not guaranteed.

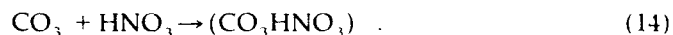
In 1985, Knop and Arnold (100) described a technique for deriving  $\text{HNO}_3$  concentrations from active chemical ionization mass spectrometer measurements rather than the passive techniques described above. Their instruments

were used on an airplane and involved an ion source located in a flow tube attached to the mass spectrometer, such as shown in Fig. 1. After ionization,  $\text{CO}_3(\text{H}_2\text{O})_n$  ions are so rapidly produced that for all practical purposes they can be considered primary ions. These ions then react with  $\text{HNO}_3$  throughout the flow tube producing  $\text{NO}_3(\text{H}_2\text{O})_n$  ions,



Knowledge of the rate constant for reaction (12), the reaction time, and the ratio of  $\text{CO}_3$ - to  $\text{NO}_3$ -containing ions yields the  $\text{HNO}_3$  concentration. The rate constant for this reaction was not known at the time but estimated to be fast, as are many reactions of this type (101). This technique could measure  $\text{HNO}_3$  concentrations sensitively throughout the atmosphere. Concentrations of  $\text{HNO}_3$  in the atmosphere are generally in the ppbv range.

Further improvement in the technique came after laboratory measurements (99) showed that the following reactions occurred in addition to reaction (12):



Knowledge of all the chemistry involved allowed a more detailed analysis to be made, although only relatively minor adjustments had to be made to the less detailed procedure. Using this technique, measurements of the  $\text{HNO}_3$  concentration have taken place on airplane, balloon, and rocket-borne instruments. The development of a rocket-borne flow tube mass spectrometer experiment shows just how far the technology has developed.

A final improvement is the use of a selected ion capillary ion source similar to that used in laboratory experiments of the MPI-K group. No measurements by this technique have yet been published. This technique allows for good control of the primary ion and opens up many of the same possibilities that have been described above for the ground-based measurements.

The examples chosen for this section are only some of the more interesting or important neutrals that have been detected by ion composition measurements. Table I lists the compounds whose concentrations have been measured by ion mass spectrometry. Also listed are the approximate altitude regions of the measurements, appropriate references, whether positive or negative ions are involved, and whether natural or man-made ions allow for the determination. For the species detected from natural ion composition measurements, the list then also refers to the ions involved; i.e., for positive ions the protonated neutral has been observed and for negative ions the deprotonated species has been observed.

Looking at Table I it is easy to see that this technique is very powerful and applies to a large number of species. The list will undoubtedly grow rapidly with such recent advances as selected ion sources and chemical titration. Derivation of neutral concentrations from ion composition measurements has also been reported from measurements higher in the atmosphere. For instance,

**Table I.** Neutrals whose concentrations have been derived from ion composition measurements in the stratosphere and troposphere.

Chemical	Altitude (km)	Detect by ion	Artificial ambient ions	Concentration range	Refs
C <sub>4</sub> H <sub>5</sub> N pyridine	0-4	-	both	1-10 pptv	48, 57, 63
CH <sub>3</sub> COCH <sub>3</sub> acetone	6-14	-	both	1-100 pptv	45, 79, 102
CH <sub>3</sub> CN acetonitrile	10-45	-	ambient	0.1-10 pptv	32, 36, 45, 53, 82, 103, 106
NH <sub>3</sub> ammonia	0-10	-	both	0.1-10 <sup>3</sup> pptv	63, 107
HOCl hypochlorous acid	35-39	-	ambient	0.1-1 ppbv	43, 71, 76
OH hydroxyl	0-11.4	-	artificial	1-10 ppbv	50, 66, 67
SO <sub>2</sub> sulfur dioxide	0-11	-	artificial	10 <sup>3</sup> -1 ppbv	50, 65
HNO <sub>3</sub> nitric acid	4-50	-	both	1-10 <sup>3</sup> pptv	37, 45, 53, 55, 71, 74, 96, 100, 108, 111, 112
H <sub>2</sub> SO <sub>4</sub> sulfuric acid	0-45	-	ambient	0.01-10 pptv	29, 31, 36, 50, 63, 66, 67, 73, 74, 76, 92, 94, 111, 113
H <sub>2</sub> O water	38-40	-	ambient	1-10 ppmv	74, 96
CH <sub>3</sub> SO <sub>3</sub> H methanesulfonic acid	0	-	both	pptv	63
C <sub>5</sub> H <sub>7</sub> N picoline	0	-	ambient	1 pptv	60
C <sub>5</sub> H <sub>7</sub> N lutidine	0	-	ambient	1 pptv	60
C <sub>3</sub> H <sub>2</sub> O <sub>4</sub> malonic acid	0	-	ambient	0.1-10 pptv	61
CH <sub>3</sub> SCH <sub>3</sub> dimethyl sulfide	0	-	artificial (fused gc)	1-100 pptv	65, 95
C <sub>10</sub> H <sub>8</sub> <i>B</i> -caradophyllene	0	-	artificial (fused gc)	1-10 pptv	65
CH <sub>3</sub> SOCH <sub>3</sub> dimethyl sulfoxide	0	-	artificial (fused gc)	1 pptv	114
NO nitric oxide	10	-	artificial	1 ppmv	112
NO <sub>2</sub> nitrogen dioxide	10	-	artificial	0.1 ppmv	112
HNO <sub>2</sub> nitrous acid	10	-	artificial	1 ppbv	112

in a recent paper, Kopp (14) has derived concentrations of H<sub>2</sub>O, CH<sub>4</sub>, H<sub>2</sub>CO, H<sub>2</sub>O<sub>2</sub>, and HCN in the mesosphere.

## V. CONCLUSIONS

The field of *in situ* ion composition measurements of the lower atmosphere is now three decades old. The first instrument was flown on October 31, 1963 (40). The distinguishing aspect of making measurements in the lower atmosphere has been the use of fast efficient pumps, necessitated because the atmospheric density is higher than that tolerated by mass spectrometers. The better part of the first two decades of this research involved understanding the basic chemistry involved. This involved not only measuring the *in situ* ion composition but also laboratory measurements of the chemistry involved. The first *in situ*

measurements were made on sounding rockets in the mesosphere and above. As better pumps for the mass spectrometers were developed, the measurements progressed lower into the atmosphere. However, it was not until 1977 (115) that measurements were made in the stratosphere, 14 years after the first mesospheric measurements. Six years later, the first tropospheric measurements were made (58, 73), leaving no more atmosphere to be explored for the first time.

In some ways this time could be considered a turning point in the measurements. No longer was the goal to delve into regions of the atmosphere previously unexplored. New goals emerged such as using the ion chemistry to derive trace neutral concentrations in a more detailed fashion. This latter goal had the effect of driving the technology to new areas. External ion sources were added, and the evolution of the ions and the neutrals involved in the earlier stages could be followed. Continual improvement is still being made with the addition of selected ion sources, chemical titration, triple quadrupoles, and gas chromatographs. While these improvements have led to a better understanding of the ambient ion chemistry, the biggest gain has been made in turning the instruments into incredibly sensitive analytical tools. Trace neutral concentrations of important atmospheric neutrals can be measured down to at least a part per quadrillion. Therefore, rather than fading in importance after three decades of research, the field of *in situ* mass spectrometric measurements is currently taking on new importance and directions.

#### ACKNOWLEDGMENTS

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